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Final Technical Report

NOVEL ELECTRON CORRELATION METHODS: MULTICONFIGURATIONAL DENSITY FUNCTIONAL THEORY

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The work we have performed in Phase I has centered upon these five tasks: partitioning of the GVB two-electron energy into Coulomb, exchange, and intra-pair terms; coding and developing GVB-RCI-DFT (post-SCF DFT on a GVB-RCI density); inclusion of self-interaction-corrected (SIC) density functionals; optimization of hybrid MCDFT methods; and generation of a preliminary version of fully self-consistent GVB-DFT. The procedure we employed to accomplish each of these tasks is described in this report, along with MCDFT results for computation of chemical properties.

Our Phase I results are highly encouraging, demonstrating that MCDFT approaches are capable of significantly improved accuracy as compared to current DFT functionals. The N^3 or better scaling with basis set size for PS-GVB's methods resulting from its use of the pseudospectral (PS) algorithm ensures that MCDFT is practical for reasonable-sized systems as well. Although considerable additional work will be required in Phase II to implement fully self-consistent MCDFT methods, find the optimum functional (or functionals), improve computational efficiency, and define protocols for utilizing GVB wavefunctions in a localized region of the molecule, the preliminary software clearly demonstrates that the basic multiconfigurational density functional theory is sound.

ACCOMPLISHMENTS AND NEW FINDINGS

A. Summary of MCDFT Methods

The theoretical approach for MCDFT methods originates with a GVB or GVB-RCI wavefunction, which adequately represents the static correlation effects necessary to obtain the correct features of a potential surface, such as left-right correlation and proper spin coupling. In the GVB approach, each bond or other electron pair is described by two non-orthogonal orbitals, whose contributions to the bond description are obtained variationally. Because PS-GVB has a high-quality automated initial guess for the wavefunction [2] and fast, reliable convergence algorithms [3], its GVB module is both highly efficient and straightforward to use. The GVB-RCI program within PS-GVB generates a correlated wavefunction from intra-pair excitations of the GVB reference wavefunction, using a highly effective contraction procedure to reduce the length of the CI expansions [4]. The program employs the pseudospectral method to speed up integral evaluation by reducing the scaling of the evaluation of each Coulomb or exchange operator in basis function space from N^4 to N^3 , and solving for the necessary matrix elements with a fast two-index transform rather than the expensive four-index transform required in traditional *ab initio* codes. The program also systematically

includes only the most important configurations to make the calculation more practical, with minimal loss of accuracy relative to the fully uncontracted expansion. The internal contraction scheme used restricts the number of CI coefficients in the RCI calculation to $\sim n^3$, where n is the number of GVB pairs, yet is in excellent agreement with a fully uncontracted CI which would contain $2^n n^3$ CI coefficients (the number of uncontracted determinants).

To add dynamic correlation energy, E_c , one can simply use the GVB or GVB-RCI charge density in DFT correlation functionals or, as a more sophisticated approach, in hybrid DFT methods, which include both GVB or GVB-RCI “exact” exchange and density functionals representing exchange as well as correlation functionals. As a modification to Becke’s theory [5] of hybrid density functional methods, we have also experimented with scaling an intra-pair GVB term (described below) as well as scaling the DFT exchange energy E_x^{NLDA} and the non-local contribution to the correlation energy E_c^{NLDA} . During Phase I, we have generated some preliminary results for the hybrid parameters and the parametrized energy partitioning required for these methods. We have also begun to implement a self-consistent version of GVB-DFT, as detailed in Section F.

Multiconfigurational density functional theory leads to improved accuracy at quite reasonable computational costs, and it can be expected to be particularly useful for various problems that are not easily studied with standard ab initio and density functional methods. For instance, transition metal chemistry is known to have large multireference effects, which may explain the marginal performance of DFT on these systems [6]. The use of an MCSCF reference also allows one to treat a number of electronic systems in which more than one determinantal wavefunction is required even in zeroth order. For example, symmetry and spin eigenstates of many of the states of a system as simple as O_2 require a multideterminantal expansion which cannot be obtained within the context of traditional density functional theory. Transition states of so-called “symmetry forbidden” reactions or the calculation of potential curves near avoided crossings involves mixing of several determinantal functions which again cannot be represented by density functional theory alone.

B. Partitioning of the GVB Two-Electron Energy into Coulomb, Exchange, and Intra-Pair Terms

The key to the performance of our MCSCF-DFT methods largely lies in the ability of the ab initio method to robustly describe dominant static correlation effects and the excellent scaling of the combined methods with basis set size. Therefore, as part of our implementation of self-consistent MCDFT methods, we have performed some of the work necessary to improve the treatment of the GVB reference wavefunction.

The partitioning of the two-electron energy into Coulomb and exchange components is not so uniquely defined for GVB or GVB-RCI wavefunctions as it is for Hartree-Fock, and in course of our Phase I work we considered different possible schemes. The issue is moot, of course, for purely “exact-exchange” methods, where the DFT correlation energy for the final GVB-RCI density is simply added to the complete final GVB-RCI energy. However, to design an accurate hybrid GVB-DFT method, in which exchange and correlation contributions from both GVB and DFT are scaled and combined, it is quite important that physically related terms are first identified in the GVB and DFT energy expressions.

Since the classical Coulomb energy of the electron density can be unambiguously defined in both the GVB and DFT approaches, it is natural to separate this from the remaining (nonclassical) exchange-correlation contributions to the two-electron energy; this is the normal approach in DFT theory, but not in MCSCF methods like GVB. The GVB energy can be rewritten so that interactions between the orbitals of a given GVB pair and all other orbitals are described by “mean-field” Coulomb and exchange operators, J_{mf} and K_{mf} . The mean-field Coulomb operator thus defined corresponds to the Coulomb operator of DFT theory. The expectation values for these operators are the classical Coulomb and mean-field exchange energies

$$J_{mf} = \sum_{i,j=1}^{N_{occ}} 2f_i f_j J_{ij} = \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\rho(\mathbf{r}_1) \rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad \text{and} \quad K_{mf} = - \sum_{i,j=1}^{N_{occ}} f_i f_j K_{ij}$$

where i and j run over all occupied orbitals and f_i is the occupation number of orbital i . For closed-shell systems, the remaining two-electron energy consists entirely of terms local to each GVB pair, and the sum of these is the intra-pair “exchange” energy, K_{gvb} ,

$$K_{gvb} = \sum_p^{n_{pair}} C_{pa}^2 (1 - C_{pa}^2) J_{pa,pa} + C_{pb}^2 (1 - C_{pb}^2) J_{pb,pb} - 4 C_{pa}^2 C_{pb}^2 J_{pa,pb} \\ - 2 C_{pa} C_{pb} (1 - C_{pa} C_{pb}) K_{pa,pb}$$

where C_{va} and C_{vb} are the CI coefficients for the natural orbitals ϕ_{pa} and ϕ_{pb} of GVB pair p . It is important to remember that K_{gvb} also describes the correlation energy of the GVB wavefunction.

With these definitions, the complete energy expression for the general open-shell (high-spin) GVB wavefunction is

$$E_{GVB} = E_{nuc} + T + J_{mf} + K_{mf} + K_{gvb} + K_{open}$$

where K_{open} contains remaining non-mean-field exchange interactions among the open-shell orbitals. The complete exchange-correlation energy of the GVB wavefunction is therefore $K_{mf} + K_{gvb} + K_{open}$. For the purpose of comparing with the DFT energy expression, $K_{mf} + K_{open}$ corresponds roughly to the Hartree-Fock exchange energy, while K_{gvb} contains components of both exchange and correlation.

To reiterate, the point of separating the non-Coulomb part of the two-electron energy in this manner is to try to isolate the exchange-like and correlation-like components of the GVB energy, so that effective hybrid methods can be defined that minimize the double-counting of exchange and correlation when DFT functionals are introduced. The aforementioned scheme represents just one possible separation. In fact, the parameterization results obtained in Phase I, while quite good, often demanded that the K_{mf} and K_{gvb} components be

scaled almost equally; this indicates to us that the K_{mf} and K_{gvb} defined here may not be physically independent and that a different separation may provide more flexibility. For instance, there are still intra-pair exchange terms $K_{pa, pb}$ in K_{mf} that can be moved into K_{gvb} . We will examine the effect of this and other partitionings in Phase II.

C. Post-SCF DFT on a GVB-RCI Density

During Phase I, we implemented GVB-RCI-DFT within PS-GVB, an effort that required computing RCI densities for a post-SCF DFT analysis. Preliminary results for post-SCF correlation-only DFT treatments showed a fairly low average error of 5.9 kcal/mol in predictions of experimental atomization energies of closed-shell systems.

We have also used the GVB-RCI-DFT software to evaluate conformational energies calculated by performing a post-SCF DFT analysis on the RCI density using various local correlation functionals. Table 1 lists the results we have obtained thus far and compares them with values obtained using GVB-RCI alone. In most cases the DFT correction results is an improvement of the RCI reference value. Given that we have not parametrized the RCI exchange and had not yet included self-interaction corrections, these results suggest that the RCI-DFT method is sound.

In Table 2, we present timings for GVB-RCI-DFT calculations on systems with up to 287 basis functions and 21 GVB pairs, using a cc-pVTZ(-f) basis set. To expedite the GVB calculations, we first converged 6-31G** wavefunctions, then used those as initial guesses for the cc-pVTZ GVB runs. The GVB calculation is clearly the rate-limiting factor of these calculations; this effect will be mitigated by our strategies to optimize GVB performance in Phase II.

The overall scaling of the GVB-RCI-DFT method is $N_{bas}^{2.95}$, which is far superior to any other common MCSCF procedure such as CASSCF. Given these timings, routine application of GVB-RCI-DFT to systems with on the order of 500 basis functions and 40 GVB pairs (80 correlated electrons) is feasible on workstations with reasonable throughput. Furthermore, not all GVB pairs need to be included in a given problem, an advantage which further extends the range of applicability of these methods.

We are continuing to address the issue of partitioning the GVB-RCI exchange term into mean field and intra-pair contributions in order to extract the analogue of the intra-pair GVB term described in Section B. Although the RCI energy expression is considerably more complicated than the GVB expression, the energy can be partitioned into Coulomb and exchange terms as well as intra- and inter-pair terms. We anticipate that for best results with hybrid methods, we will then need to scale this intra-pair RCI term, as we did for GVB-DFT.

D. Correlation Functional Modifications

We have found, as have others [7, 8, 9], that a correlation correction calculated with standard DFT correlation functionals using the GVB density leads to an over-correction of the correlation energy. For example, an atomization calculation of C_2H_4 has a GVB value of

Molecule	RCI	RCI-VWN	RCI-VWN5	RCI-PZ81	Exp.
cyclohexanol	1.04	0.93	0.49	0.47	0.52
piperidine	0.86	0.87	0.87	0.87	0.40
2,3-dimethylbutane	0.03	0.04	0.03	0.03	0.17
N-methylformamide	0.97	1.10	1.09	1.08	1.45
butane	1.16	0.97	1.00	1.00	0.75
methyl acetate	8.61	8.71	8.73	8.71	7.5-8.5
methyl ethyl ether	1.71	1.55	1.58	1.58	1.50
acrolein	1.82	1.73	1.75	1.75	2.00
isopropylamine	0.31	0.43	0.41	0.41	0.45
propionaldehyde	0.64	0.83	0.80	0.80	0.95
methyl formate	4.97	5.36	5.31	5.30	4.75
ethyl ether	1.87	1.53	1.60	1.60	1.10
1-butene	0.72	0.41	0.45	0.45	0.53
2-butene	1.89	1.68	1.72	1.71	1.00
butanone	1.09	1.27	1.24	1.24	1.15
1,3-butadiene	2.49	2.45	2.47	2.46	2.49
methyl vinyl ether	0.38	0.81	0.75	0.75	1.15
cyclohexamine	1.42	0.76	0.89	0.89	1.10

Table 1: Conformational energies in kcal/mol, evaluated with GVB-RCI only (RCI) and by performing a post-SCF DFT analysis of the GVB-RCI self-consistent wavefunction using various local correlation functionals.

Molecule	N _{bas}	N _{pair}	6-31G**	cc-pVTZ	RCI Int.	RCI Energy	DFT	Total
Methylcyclohexane	287	21	76	550	110	6	142	884
Cyclohexane	246	18	43	340	68	3	86	540
Methylvinylether	146	12	12	83	10	0.5	13	119

Table 2: CPU times (minutes) for pseudospectral GVB initial wavefunction calculations with the 6-31G** basis and with the cc-pVTZ(-f) basis using the 6-31G** results as initial guesses, RCI integral generation, RCI energy solver, and DFT correlation energy treatment of the GVB-RCI density. All calculations performed on a single IBM-SP2 390 thin node.

461.4 kcal/mol and a VWN correlation functional corrected value of 581.1 kcal/mol, in comparison to the correct atomization energy of 531.9 kcal/mol.

There are two established methods for dealing with this over-correlation that need to be implemented and tested within the GVB-DFT and GVB-RCI-DFT formalisms: modifying the spin part of the density interactions, and modifying the total spin-space density that enter into the correlation functionals. Although we originally slated work on both of these methods for Phase II, we have partially completed programming and testing one of these approaches, the inclusion of "self-interaction-corrected" (SIC) functionals [7, 10] within the code. These functionals assume that the dominant correlation effect is between electrons of opposite spins and thus subtract out the correlation from like spins, writing the DFT correlation correction to the energy E_c as:

$$E_c = \int dr \rho(r) \epsilon_c[\rho_\alpha(r), \rho_\beta(r)] - \int dr \rho_\alpha(r) \epsilon_c[\rho_\alpha(r), 0] - \int dr \rho_\beta(r) \epsilon_c[0, \rho_\beta(r)]$$

where ρ_α and ρ_β denote the $\alpha\alpha$ and $\beta\beta$ parts of the total spin density $\rho = \rho_\alpha + \rho_\beta$ and $\epsilon_c[\rho_\alpha(r), \rho_\beta(r)]$ is a standard correlation functional. This approach could be further parametrized by scaling (with a factor of 0 to 1) the part of the self-interaction which is subtracted in the above equation. Note that without the SIC correction, the H atom has an unphysical non-zero DFT correlation energy. Part of the rationale for this approach is that the treatment of ab initio (HF or GVB) exchange interactions is providing for a large fraction of the $\alpha\alpha$, $\beta\beta$ correlations and hence this correlation should be removed from E_c as above.

Some preliminary results for atomization energy calculations generated using the new SIC code are included in Section E.2 below. In Phase II, we will continue to study the performance of such SIC modifications for various correlation functionals and in conjunction with the exchange scaling schemes discussed in Section E.

E. Optimization of Hybrid MCDFT Methods

E.1. Conformational Energy Calculations

The "three parameter" method that was developed by Becke [5] and is now widely used for density functional theory calculations was designed to give good self-consistent DFT results by combining optimal amounts of "exact" Hartree-Fock and density functional terms. The parameters were chosen by performing least-squares fitting to obtain the values that yielded the best results for chemical properties of several dozen molecules. Popular hybrid methods that use these three parameters include B3LYP.

Because Becke's parametrization was designed to allow the DFT treatment to account for effects neglected by Hartree-Fock, we did not expect the parameters to be ideal for post-SCF DFT analysis of GVB wavefunctions or for self-consistent GVB-DFT. In Phase I, we performed a preliminary analysis of what these parameters should be to give best results for GVB-DFT and found that re-fitting the parameters gave a dramatic improvement for post-SCF DFT calculations on GVB wavefunctions, regardless of the local and non-local correlation functionals used.

Our preliminary GVB-DFT parametrization was designed to minimize RMS errors for a set of 17 conformational energy differences, where the cases and their experimental values were drawn from among papers concerning calculation of relative conformational energies by Murphy et al. [11] and St.-Amant et al. [12]. The conformational energy calculations were performed with our electronic structure software, PS-GVB, using a cc-pVTZ(-f) basis set, an energy convergence criterion of 1.0×10^{-6} Hartrees, and PS-GVB's highest-accuracy setting. The DFT exchange-correlation energy was calculated non-self-consistently using the self-consistent GVB density; all GVB calculations included all possible sigma and pi bond pairs.

The RMS error obtained for pure GVB conformational energy differences, 0.43 kcal/mol, was considerably lower than the HF or B3LYP RMS errors of 0.52 and 0.54 kcal/mol, and including a treatment of the GVB densities with correlation functionals yields markedly improved RMS errors (0.32 kcal/mol for GVB-LYP, for instance, an improvement of more than 30% over the pure HF or B3LYP results). However, applying the hybrid DFT method B3LYP to the GVB densities gave a quite poor RMS error of 0.56 kcal/mol. Clearly the weights assigned to various terms by Becke's three parameters were unsuitable for our GVB-DFT conformational energy calculations.

Results of our Phase I parametrization of GVB-DFT hybrid methods are summarized in Table 3. We first performed a completely unrestricted parameter fit to minimize the RMS error, analyzing coefficients for *every* GVB and DFT term, with no restrictions on the range of the coefficients. During this fit, we allowed the coefficients for the exact exchange terms K_{mf} and K_{gvb} (described in Section B) to vary separately. As we expected and as Table 4 shows, the resultant coefficients were totally unphysical, but this fitting gave us an idea of the best result we could possibly expect for an RMS conformational energy difference error for the data set in question, using only GVB and post-SCF DFT terms: an RMS error of 0.23 kcal/mol, considerably lower than the GVB and RMS error of 0.43 and less than half the B3LYP error of 0.56. The terms from the local correlation functional using the GVB density are clearly the most important for a good fit to experimental data. The unrestricted fit also makes it clear that the Slater local exchange functional [13], whose coefficient is very small, is contributing nothing useful to the fit: the GVB exact exchange dominated the calculation of exchange energy. Therefore, for the remaining fittings, we eliminated the Slater contribution.

	Pure SCF		Post-SCF DFT on GVB density											
			Single functional			Parametrized combination of functionals								
	GVB	B3LYP	VWN	LYP	GGA-IIc	B3LYP	unrestricted	$K_{mf}=1$	VWN/P86	PW91/P86	VWN/GGAIIc	PW91/GGAIIc	VWN/LYP	PW91/LYP
Error:	0.43	0.54	0.33	0.32	0.34	0.56	0.23	0.30	0.31	0.31	0.31	0.31	0.30	0.31

Table 3: RMS errors in kcal/mol for calculations of 17 conformational energy differences using various SCF and post-SCF DFT methods. Coefficients used for parametrized combinations of functionals are shown in Table 4 and Table 5.

Fitting Conditions	K_{mf}	K_{gvb}	Slater	Becke88	VWN	PW-91	LYP	Perdew86	GGA-IIc
unrestricted	1.3014	0.9530	-0.2031	-7.0147	104.19	-116.42	-2.6362	-24.585	12.282
$K_{mf}=1$	1.0000	0.9477	0.0000	0.5497	1.0000	0.7813	0.5628	0.5265	0.0000

Table 4: Coefficients for various terms for parameter fitting to reduce RMS errors for conformational energy differences described in the text. The $K_{mf}=1$ fit also restricted all other coefficients to be between 0 and 1.

When we constrained the K_{mf} coefficient to unity and restricted the other coefficients to be between 0 and 1, while still allowing all possible functionals to contribute, the RMS error was 0.30, still much lower than GVB or B3LYP alone gave. However, as Table 4 shows, the total coefficients for each type of exchange or correlation term were too high. In addition, including a contribution from every functional available would be difficult to justify as a general method.

Our next goal was to restrict the parameters to reasonable values and definitions without significantly reducing the accuracy of the GVB-DFT results. We followed the model provided by Becke’s three parameters, restricting the sum of the parameters for total exact exchange and local exchange to 1 (in this case by including all of the GVB K_{mf} exchange energy and leaving out the Slater term), and ensuring that the parameters for local correlation also summed to 1. Parameters for Becke’s 1988 gradient correction to the exchange [14] and for a non-local correlation functional were allowed to vary between 0 and 1. (As usual, when LYP was used as a non-local correlation functional, the local correlation functional’s contribution was reduced correspondingly to make up for the local correlation contribution of the LYP functional.) We also introduced another parameter for the GVB intra-pair term K_{gvb} , which is described in detail in Section B. In summary, we were fitting for the α , β , and χ that would give the lowest RMS energy error for energies of the form:

$$E^{GVB-DFT} = E_{Coulomb}^{GVB} + E_{xmf}^{GVB} + \alpha E_{intra-pair}^{GVB} + \beta E_x^{NLDA}[\rho(\psi_{gvb}), \nabla\rho(\psi_{gvb})] \\ + E_c^{LDA}[\rho(\psi_{gvb})] + \chi E_c^{NLDA}[\rho(\psi_{gvb}), \nabla\rho(\psi_{gvb})]$$

while restricting all three parameters to be between 0 and 1. We optimized these parameters for six different cases, where for each individual case, we chose either VWN [15] or PW-91 [16] as the local correlation functional and either LYP [17], Perdew 86 [18], or GGA-IIc [16] as the non-local correlation functional.

Ideally, we wanted our results to be nearly as accurate as the 0.30 RMS error we had obtained with the minimal constraints described above, and to remain relatively stable with our choice of functional, particularly in regard to the local correlation functional, which is not scaled by any variable parameter. We also felt the β parameter should be low, since the Becke gradient correction is really meant to address the limitations of the Slater exchange functional and should therefore be unnecessary when only the accurate GVB exchange is used instead.

Finally, we wanted the GVB intra-pair scaling parameter to be consistent for the various functional choices.

As Table 5 indicates, all of these conditions were met: the RMS error ranged from 0.30 to 0.31 kcal/mol over all six cases, the value obtained for β in every case was 0, and the value for χ was always 0.94. This preliminary work should provide a solid foundation for further

	VWN/ P86	PW91/ P86	VWN/ GGAIc	PW91/ GGAIc	VWN/ LYP	PW91/ LYP
α	0.94	0.94	0.94	0.94	0.94	0.94
β	0.00	0.00	0.00	0.00	0.00	0.00
χ	0.25	0.33	0.29	0.40	0.42	0.54
RMS Error	0.31	0.31	0.31	0.30	0.31	0.30
MA Error	0.24	0.24	0.24	0.23	0.23	0.23

Table 5: Parameters fitted for various combinations of functionals for post-SCF DFT calculations, and the resultant RMS and mean absolute errors (in kcal/mol) for conformational energy difference calculations. Parameters are described in the text.

parametrization efforts in Phase II.

E.2. Atomization Energy Calculations

Our Phase I calculations of GVB-DFT atomization energies for 44 molecules from the G2 data set [19] further demonstrate the promise of MCDFT methods, although much work still remains to be done in Phase II to optimize hybrid method parameters and other aspects of GVB-DFT and GVB-RCI-DFT calculations. All of our preliminary atomization energy calculations described here used the cc-pVTZ(-f) basis set and PS-GVB’s highest accuracy setting, starting with the standard initial-guess GVB wavefunction. For the first set of calculations described here, those without self-interaction-corrected functionals, GVB pairs were defined for all molecular bonds, but not lone pairs, while atoms were treated at the ROHF level; for the calculations with self-interaction corrections, GVB lone pairs were also included.

We first evaluated the effects of various functionals in the post-SCF DFT treatment of HF and GVB wavefunctions. The use of local and non-local DFT correlation functionals uniformly gave a dramatic improvement over the straight HF and GVB atomization energies, as is shown in Table 6. However, the *unscaled* inclusion of the Slater local exchange functional and Becke non-local gradient correction to the exchange (BLYP, for example) actually made the GVB-based results worse, although the HF-based atomization energies again improved substantially. We did ultimately obtain higher quality results for the GVB-based treatment when including DFT exchange functionals, but only by retaining some fraction of the GVB exchange energy in hybrid methods or by using SIC functionals. Some of our results for hybrid methods are included in Table 6 for comparison; the methods are explained in detail below.

	SCF wavefunction	DFT correlation functional(s)	DFT exchange functional(s)	DFT hybrid method	atomization energy error
<i>Pure</i>	HF	—	—	—	80.3
	GVB	—	—	—	49.7
<i>Post-SCF Correlation Only</i>	HF	VWN (local) only	—	—	26.0
	GVB	VWN (local) only	—	—	23.7
	HF	PW91 (local) only	—	—	28.6
	GVB	PW91 (local) only	—	—	22.8
	HF	GGA-II (non-local) only	—	—	25.2
	HF	LYP (non-local) only	—	—	25.6
	GVB	GGA-II (non-local) only	—	—	17.2
	GVB	LYP (non-local) only	—	—	18.4
<i>Post-SCF Exchange & Correlation</i>	HF	GGA-II (non-local) only	GGA-II	—	5.1
	HF	LYP (non-local) only	Slater/Becke	—	5.3
	HF	VWN (local) / LYP (non-local)	Slater/Becke	B3LYP	5.0
	GVB	GGA-II (non-local) only	GGA-II	—	26.4
	GVB	LYP (non-local) only	Slater/Becke	—	30.7
	GVB	VWN (local) / LYP (non-local)	Slater/Becke	B3LYP	19.8
<i>Post-SCF with New Hybrid Method</i>	GVB	VWN (local) / Perdew86 (non-local)	Slater/Becke	new	4.06
	GVB	PW91 (local) / Perdew 86 (non-local)	Slater/Becke	new	4.11
	GVB	VWN (local) / GGA-IIc (non-local)	Slater/Becke	new	3.36
	GVB	PW91 (local) / GGA-IIc (non-local)	Slater/Becke	new	3.73
	GVB	VWN (local) / LYP (non-local)	Slater/Becke	new	3.45
	GVB	PW91 (local) / LYP (non-local)	Slater/Becke	new	3.36

Table 6: Full comparison of mean absolute errors (in kcal/mol) for atomization energy calculations on 50 molecules from the G2 data set using various ab initio methods. All DFT calculations were post-SCF treatments of the DFT energy using the density from the given self-consistent wavefunction. New hybrid methods are explained later in this section. Entries of — mean no, none, or not relevant.

Hybrid methods we considered contained various proportions of the GVB mean-field exchange energy, the GVB intra-pair energy, the Slater local exchange functional, the Becke non-local exchange functional, the VWN and Perdew-Wang 1991 local correlation functionals, and the Perdew 1986, GGA-II and LYP non-local correlation functionals. We first tried to optimize only the α , β , and χ parameters described in Section E.1, leaving out the

Slater exchange functional term (and including all of the K_{mf} GVB exact exchange), and parametrizing for various combinations of one local and one non-local correlation functional. The resultant RMS errors were reasonable, but somewhat disappointing, ranging from 15-20 kcal/mol depending on the functional choices.

Noting that the large RMS error of 53.4 kcal/mol for the GVB-only calculations might indicate problems with the GVB reference wavefunctions, we next allowed a non-zero contribution for the Slater exchange, subtracting off a corresponding amount of the exact exchange. The intra-pair term was still allowed to vary independently. The total GVB-DFT energy was thus taken to be

$$E^{GVB-DFT} = E_{Coulomb}^{GVB} + c_x E_{kmf}^{GVB} + (1 - c_x) E_x^{Slater} [\rho(\psi_{gvb})] + \alpha E_{intra-pair}^{GVB} + \beta E_x^{NLDA} [\rho(\psi_{gvb}), \nabla \rho(\psi_{gvb})] + E_c^{LDA} [\rho(\psi_{gvb})] + \chi E_c^{NLDA} [\rho(\psi_{gvb}), \nabla \rho(\psi_{gvb})]$$

where we constrained all four parameters (c_x , α , β , and χ) to be between zero and one. The RMS errors improved dramatically for all hybridization schemes examined, as shown in Table 7.

	Pure SCF		Post-SCF DFT on GVB density									
			Single functional			Parametrized combination of functionals						
	GVB	B3LYP	VWN	LYP	GGA-IIc	B3LYP	VWN/P86	PW91/P86	VWN/GGA-IIc	PW91/GGA-IIc	VWN/LYP	PW91/LYP
RMS Error:	53.4	3.5	27.8	23.7	22.5	19.8	4.95	5.00	4.57	4.66	4.43	4.46

Table 7: RMS errors in kcal/mol for atomization energy calculations for 44 molecules using various SCF and post-SCF DFT methods. Coefficients used for parametrized combinations of functionals are shown in Table 8.

The optimized parameters for the various hybrid functionals, shown in Table 8, show a number of notable trends. The α and c_x coefficients for the GVB mean-field exchange and intra-pair terms are quite similar for each individual method, as seen also in the conformational energy difference study; this may indicate that our current separation of these components has not yet isolated two physically distinct contributions to the total GVB exchange-correlation energy. Unlike the conformational energy study, here a large proportion of the Slater exchange energy was required to achieve best results, which previously were only comparable to that in the standard B3LYP parameterization. (We note that Becke's three-parameter method was optimized to produce good atomization energies using molecules from this same data set, which probably explains why its performance was fairly bad for the conformational energies we considered yet quite good for these atomization energies.)

	B3LYP	VWN/ P86	PW91/ P86	VWN/ GGAIIc	PW91/ GGAIIc	VWN/ LYP	PW91/ LYP
c_x	0.20	0.16	0.18	0.23	0.22	0.30	0.30
α	0.20	0.18	0.19	0.24	0.24	0.31	0.36
β	0.72	0.30	0.20	0.31	0.20	0.24	0.22
χ	0.81	0.00	0.00	0.29	0.20	0.73	1.00
RMS Error	19.8	4.96	5.00	4.57	4.66	4.43	4.46
MA Error	17.5	4.06	4.11	3.36	3.73	3.45	3.36

Table 8: Parameters fitted for various combinations of functionals for post-SCF DFT calculations, and the resultant RMS and mean absolute errors (in kcal/mol) for atomization energy calculations. Parameters are described in the text.

With the Phase I implementation of a self-interaction-corrected VWN local correlation functional, as described in Section D, we reevaluated atomization energies for a smaller set of 16 of the G2 molecules that contained only hydrogen, carbon, nitrogen, and oxygen. For these calculations, we also included GVB lone pairs as well as GVB bond pairs. Table 9 shows that

	SCF wavefunction	DFT correlation functional(s)	DFT exchange functional(s)	DFT hybrid method	mean absolute error	RMS error
<i>Pure SCF</i>	GVB	none	none	none	62.9	66.4
	SCF B3LYP	VWN / LYP	Slater / Becke	B3LYP	1.4	2.0
<i>Post-SCF DFT</i>	GVB	VWN (SIC) only	none	none	14.2	19.0
	GVB	VWN (SIC) / LYP	Slater / Becke	B3LYP	20.2	21.9
	GVB	VWN (SIC) / LYP	Slater / Becke	new (SIC)	1.3	1.8

Table 9: Full comparison of mean absolute and RMS errors (in kcal/mol) for atomization energy calculations on 16 molecules from the G2 data set using various methods, where the VWN local correlation functional was self-interaction-corrected (SIC) where indicated. All post-SCF DFT calculations used the self-consistent GVB density, as indicated. New parameters used for last calculation listed were $c_x=0.12$, $\alpha=0.25$, $\beta=0.42$, and $\chi=0.08$, where these parameters are as described earlier.

B3LYP performs particularly well for these molecules, while GVB’s performance is not especially good; nevertheless, the *highest* accuracy obtained is for a post-SCF DFT treatment of the GVB density, even for this preliminary, non-self-consistent version of the method, an extremely encouraging result.

We are confident that our Phase II improvements, which will include modification of the GVB reference wavefunction, further development of the self-interaction-correcting DFT functional code, and, especially, full implementation and parametrization of self-consistent GVB-DFT computations, will reduce errors still further. We found that the self-consistent HF-B3LYP mean absolute error for these atomization energy calculations is about half that resulting from a post-SCF B3LYP treatment of HF wavefunctions, demonstrating the importance of a self-consistent treatment.

F. Self-Consistent GVB-DFT: Theory and Preliminary Results

In order to efficiently optimize accurate molecular structures with the GVB-DFT and GVB-RCI-DFT methods, and to calculate wavefunction-dependent properties such as multipole moments, polarizabilities, hyperpolarizabilities, it is necessary that the wavefunction be calculated self-consistently.

Although we originally planned to implement a self-consistent GVB-DFT method only during Phase II, our progress in Phase I encouraged us to investigate the advantages of a completely self-consistent treatment as soon as possible. Therefore, we have completed a preliminary version of this software, specialized to closed-shell systems and "exact-exchange" methods, in which the DFT exchange-correlation functional is used in the refinement of the GVB orbitals and CI coefficients. To our knowledge, this is the *only* existing software with this capability.

In a GVB wavefunction, each GVB electron pair, p , is described by a pair of natural orbitals ψ_{pa} and ψ_{pb} , and their CI coefficients, C_{pa} and C_{pb} (where $C_{pa}^2 + C_{pb}^2 = 1$). To optimize the GVB wavefunction, a separate Fock matrix is defined for the core (non-GVB) orbitals and for each GVB natural orbital and open-shell orbital [20]. The addition of the DFT exchange-correlation energy to the GVB energy expression modifies the normal GVB Fock matrices by adding the DFT exchange-correlation potential to each Fock matrix; the Fock matrix, F_p , for orbital i is

$$F_i^{GVB-DFT} = F_i^{GVB} + f_i V^{xc},$$

where f_i is the occupation of the orbital i ($f_i = C_i^2$ for GVB natural orbital ψ_i) and V^{xc} is the DFT exchange-correlation potential.

The CI coefficients are optimized at each iteration to minimize the total energy of the wavefunction. Normally this can be done by solving a simple quadratic equation for the coefficients for each GVB pair in turn, and iterating over the complete set of GVB pairs until self-consistency is reached. When the complete GVB two-electron energy is included in the GVB-DFT energy, the equations for the CI coefficients are only slightly modified in the presence of the DFT exchange-correlation terms. When the GVB exchange energy is scaled, however, as in a hybrid method such as B3LYP, a fourth-order equation must be solved for the CI coefficients for each pair. This equation and its component terms take the form

$$\alpha^4 Y_{ab}^p + \alpha^3 \left(2 \left(Y_{bb}^p - Y_{aa}^p \right) - 2 \left(Z_{ab}^p - Z_{bb}^p \right) \right) + \alpha \left(2 \left(Y_{bb}^p - Y_{aa}^p \right) + 2 \left(Z_{ab}^p - Z_{aa}^p \right) \right) - Y_{ab}^p = 0$$

$$Y_{aa}^p = 2h_{pa,pa}^0 - V_{pa,pa}^{xc} + 2 \sum_{j \neq pa,pb} f_j (2J_{j,pa} - K_{j,pa}) + xJ_{pa,pa}$$

$$Y_{ab}^p = xK_{pa,pb}$$

$$Z_{aa}^p = 2(1-x)J_{pa,pa}$$

$$Z_{ab}^p = 4(1-x)J_{pa,pb}$$

Here, x is a coefficient that scales the GVB exchange energy (both K_{mf} and K_{gvb}); similar equations are obtained when the mean-field and intra-pair energies are scaled independently. For $x=1$, the “exact exchange” limit, the Z terms vanish and the usual quadratic equation for α is obtained. For $x=0$, both K_{mf} and K_{gvb} are completely removed and the GVB wavefunction collapses to a single Slater determinant, because the DFT exchange-correlation energy does not provide the intra-pair interactions required to stabilize a multi-configuration wavefunction. Therefore, any hybrid functional defined for use in a self-consistent GVB-DFT theory must retain some amount of the GVB intra-pair exchange interaction, or it reduces to a canonical DFT theory.

Solution of these equations is straightforward, and may be simplified by using the root of the corresponding quadratic equation as an initial guess. These equations also make it clear that if the intra-pair energy, K_{gvb} , is completely scaled away, then the only the lower-energy natural orbital in each pair is populated and the GVB wavefunction collapses to a single-determinant HF wavefunction.

The extension of these equations to open-shell systems is easily done. Open shell systems are treated in DFT theory analogously to the unrestricted Hartree-Fock method, with separate exchange-correlation potentials V_{α}^{xc} and V_{β}^{xc} for the alpha and beta spin-orbitals. To use these terms in the context of the explicitly restricted GVB theory, we will employ the standard relationships to recombine them into restricted core and open-shell potentials, V_{closed}^{xc} and V_{open}^{xc} ,

$$V_{closed}^{xc} = \frac{1}{2} \left(V_{\alpha}^{xc} + V_{\beta}^{xc} \right), \quad V_{open}^{xc} = \frac{1}{2} V_{\alpha}^{xc}$$

V_{closed}^{xc} is then used in the Fock matrices for the core and GVB pair orbitals, while V_{open}^{xc} is used for the open-shell Fock matrix.

We have implemented the self-consistent GVB-DFT theory described above for closed-shell systems and “exact exchange” methods and have obtained encouraging results for the handful of cases that we have examined. Convergence of the hybrid GVB-DFT wave-

function to self-consistency appears to be reliable using the standard GVB-DIIS [3] and OCBSE [20] convergence schemes available in PS-GVB, both when starting from PS-GVB's default GVB initial guess and when starting from a converged GVB wavefunction.

Table 10 and Table 11 show preliminary results from three systems in our conformational energy database. In these systems there is little additional lowering of the total GVB-DFT energy, when compared with the non-self-consistent post-SCF DFT treatment, and no impact on the accuracy of the conformational energy differences. When the open-shell version

Method	formic acid		1-butene		isoprene	
	(c)	(t)	(s)	(c)	(g)	(t)
GVB	-188.974709	-188.967843	-156.346391	-156.344988	-194.236185	-194.238324
Post-SCF DFT	-191.070371	-191.063307	-158.945255	-158.944344	-197.346524	-197.348978
SCF GVB-DFT	-191.070934	-191.063888	-158.947068	-158.946146	-197.348647	-197.351088

Table 10: Conformational energies in atomic units for three representative systems, using GVB, GVB-DFT with a post-SCF DFT treatment, and our preliminary self-consistent GVB-DFT software.

Method	formic acid	1-butene	isoprene
GVB	4.31	0.88	1.34
Post-SCF DFT	4.43	0.57	1.54
SCF GVB-DFT	4.42	0.58	1.53
Exp. Value	3.90	0.53	2.65

Table 11: Conformational energy differences in kcal/mol for three representative systems, using GVB, GVB-DFT with a post-SCF DFT treatment, and our preliminary self-consistent GVB-DFT software.

of this code becomes available, we will be able to calculate atomization and bond dissociation energies, in which the impact of a fully self-consistent treatment should be greater (for instance, the RMS error for the atomization energies of the G2 database molecules is halved for the standard B3LYP functional when it is applied self-consistently versus as a post-SCF method).

These preliminary results are encouraging because they suggest that, for at least some molecular properties, almost all of the accuracy of the GVB-DFT theory can be obtained by an inexpensive post-SCF DFT treatment. Also, when a self-consistent calculation is required, as for the calculation of analytic gradients, it should be possible to devise a more efficient self-consistent procedure by incorporating the DFT exchange-correlation potential in the SCF

equations only after the orbitals have been largely converged by the faster standard GVB method.

In Phase II, we will complete the development of the SCF-GVB-DFT software described here by extending it to open-shell systems and mixed "exact exchange"/DFT methods. This will be the basis for implementing analytic gradients for the GVB-DFT wavefunction, allowing optimization of equilibrium geometries and transition states at this level of theory. Existing molecular properties methods currently available for standard GVB wavefunctions will be extended to GVB-DFT wavefunctions as well.

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PERSONNEL SUPPORTED

Schrödinger scientists Dr. Robert B. Murphy, Dr. W. Thomas Pollard, and Dr. Jean-Marc Langlois performed the work described in this report, under the management of Schrödinger's President, Dr. Murco Ringnalda.

PUBLICATIONS

No publications have yet been completed or submitted for this project.

INTERACTIONS/TRANSITIONS

Preliminary results for some GVB-DFT and GVB-RCI-DFT calculations were presented by Dr. Jean-Marc Langlois at the American Conference on Theoretical Chemistry in Salt Lake City, Utah in the summer of 1996.

DISCOVERIES, INVENTIONS, PATENT DISCLOSURES, OR HONORS/AWARDS

None.